

IS

Sample & Analysis

This document provides general background information on the sampling and analysis of the various forms of cyanide in aqueous samples at gold mining operations. It is not intended to be an all-inclusive reference for cyanide sampling or analysis.

General Information

This document places emphasis on proven and reliable methods used globally for the monitoring of process solutions and environmental compliance at gold mining operations. Other analytical procedures do exist for the measurement of cyanide that are capable of generating acceptable results; these alternative procedures can be substituted for the traditional methods included in this document. The mining industry, regulators and most service laboratories generally use the following guidelines for cyanide species.

Free Cyanide (CN_F)

Only hydrogen cyanide and the cyanide ion in solution can be classed as "free" cyanide. The proportions of HCN and CN^- in solution are according to their equilibrium equation; this is influenced by the solution pH.

Methods used to detect free cyanide should not alter the stability of weaker cyanide complexes, as they may otherwise be included in the free cyanide result. Methods used to detect free cyanide should be clear of interferences due to the presence of high concentrations of more stable cyanide complexes or other cyanide forms. If not, the interference must be quantified and allowed for in the result.

Weak Acid Dissociable Cyanide (CN_{WAD})

Unlike the definition of "free cyanide" which identifies the specific cyanide species being measured, WAD cyanide refers to those cyanide species measured by specific analytical techniques. WAD cyanide includes those cyanide species liberated at moderate pH of 4.5 such as HCN(aq) and CN^- , the majority of Cu, Cd, Ni, Zn, Ag complexes and others with similar low dissociation constants.

Methods used to measure WAD should be free from interferences due to the presence of high concentrations of more stable cyanide complexes or other cyanide forms. If not, the interference must be quantified and allowed for in the result.

Total Cyanide (CN_T)

This measurement of cyanide includes all free cyanide, all dissociable cyanide complexes and all strong metal cyanide including ferro-cyanide $Fe(CN)_6^{4-}$, ferri-cyanide $Fe(CN)_6^{3-}$, and portions of hexacyano cobaltate $Co(CN)_6^{3-}$ and those of gold and platinum. Only the related or derived compounds cyanate (CNO^-) and thiocyanate (SCN^-) are excluded from the definition of total cyanide.

Methods used to determine total cyanide must be shown to be capable of quantitatively determining all stable complexes of cyanide, including the cobalt cyanide complex. If methods determine other analytes as well (e.g. include SCN^-), those analytes need to be determined separately and allowed for in the total result.

Sampling

The importance of sampling and sample handling, prior to delivery to the laboratory, is summarized by the following statement.

The results of analysis can be no better than the sample on which it was performed.

While the taking of either aqueous or solid samples may appear easy, the collection of correct samples, both in terms of location and with respect to the analytes to be monitored, is fraught with difficulties. Any sampling must have as its aim the collection of a representative portion of the substance to be analysed. When this

portion is presented for analysis, the parameters to be determined must be present in the same concentration and chemical or biological form as found in the original environment from which the portion was removed.

Samples representative of a site, or of a portion of a site, provide information that is often extrapolated to include the whole area under investigation. This is true whether the entity being sampled is a contaminated section of land, surface water, an industrial outfall, or a drum containing waste material. Therefore, samples must be representative of the specific entity being sampled, but not necessarily representative of the entire area of which it is part.

The overall objectives of a sampling program must be considered in the development of the sampling plan. Sampling may be performed for one of several purposes:

Maximum, minimum and average values for a near steady state stream with the aim of monitoring compliance versus set specifications (process control, environmental criteria). Such data can illustrate the likelihood and magnitude of occurring non-compliance provided enough data points have been analyzed from samples. Process, residue, and effluent stream analysis could have this type of objective. Even aquifer sampling (bore-holes) would fit this description. Often the relative mass-flows have to be known for proper data integration.

Maximum, minimum and average values derived from the analysis of "batch streams" such as treated backfill portions or detoxified waste batches usually require a minimum of one data point per batch to insure a representative sample. The major objective remains one of compliance and/or verification of effective management procedures for the batch streams involved.

1. Non-steady state events following a cyclic pattern are often influenced by several parameters, and these parameters in themselves may also be susceptible to cyclic changes. In other words, these confounding factors create a complex situation that requires careful analysis and planning to obtain a representative sample.

2. The cycle periods have to be known along with many other factors of influence in the "system". A typical example would be the sampling of tailings surface liquid (or solids), decant liquids or return dam bulk liquid. All of these "sample populations" undergo massive cyclic fluctuations through influence of chemical and physical changes from process management tailings surface events and seasonal climatic conditions.

3. It will be apparent that the cycle periods are not in any way synchronized and hence seemingly random data might be obtained. An objective for such sampling campaigns could be the establishment of a predictions database based on the understanding of the fundamental principles. This means that a complete, non-biased sampling effort across the longest cycle needs to be performed at least once. Alternatively, once such principles are known, selected samples taken at certain times could be analyzed for monitoring purposes. While many sampling strategies may be developed, the main, basic approaches to sampling are depicted in the following table.

Approach	Number of Samples	Potential Relative Bias	Basis of Site Selection
Judgemental	Small	Very Large	Prior history, visual assessment, and/or technical judgement
Systematic	Large	Small	Consistent grid or pattern
Random	Very Large	Very Small	Simple random selection

Sample Preservation

Once samples are removed from their natural environment, chemical or biological reactions can occur to change the composition of the sample, so it is best to analyze the sample as quickly as possible. Preservation of the sample will keep the parameter of interest in the same form as it was prior to the removal from its surroundings. No single preservation technique will preserve all parameters, so each parameter of interest must be considered and preserved specifically. While most soil samples require exclusion of light, air and warmth to preserve the integrity of the sample, aqueous samples require a more concerted effort.

Samples of aqueous cyanide species are potentially very reactive and toxic, so safety precautions such as gloves and protective clothing must be rigorously observed. Due to their reactivity, sample solutions must be

tested on site prior to cyanide analysis to preserve them against the main interfering substances, oxidizing matter and sulfides.

The presence of oxidizing matter is detected by potassium iodide/starch test papers. Place a drop of the sample on a moist test paper strip. A blue coloration of the test paper indicates the presence of sufficient oxidizing matter to potentially react with the cyanide present during transport. Oxidizing agents must be reduced prior to sending the sample to the laboratory.

Procedure for Removal of Oxidizing Matter

1. Remove and retain any solids by decantation or pressure filtration.
2. Add sodium arsenite and mix. About 0.1g/L is usually sufficient.
3. Retest, and if test strip is discolored, retreat as per Step 2.
4. Return solids to sample solution and raise pH to 12 by adding 1-2 pellets of solid sodium hydroxide.

The presence of sulfides is indicated by lead acetate paper turning black. Place a drop of the sample on the test paper previously moistened with a drop of acetic acid and if the paper darkens, sulfides are indicated. Sulfides are removed by reaction with lead carbonate.

Procedure for Removal of Sulfides

1. Remove any solids by decantation or pressure filtration and hold.
2. Add lead carbonate (about 0.1 g/L) and mix.
3. Remove formed lead sulfide by pressure filtration and discard PbS precipitate.
4. Retest sample solution. If test strip is discolored, retreat as in Steps 2 and 3.
5. Return solids to sample and raise pH to 12 with solid sodium hydroxide.

Samples should be stored in a dark place at about 4 C, such as in an esky (cool box) during transport and then refrigerated at the laboratory. Soil samples for cyanide analysis (in cores or jars) must be wrapped in dark plastic and kept cool at 4 C without further treatment.

Transport and Storage

Once correctly preserved and packaged, samples should be sealed and each container (bottle or jar) individually placed in a sealed plastic bag. All samples should then be packed in an esky (cool box with some ice bricks) to keep them cool during transport. Shipment to the analytical laboratory should occur as soon as practical by overnight truck or airfreight courier. It is essential that the sampling protocol be recorded and a chain of custody included with the shipment to allow tracking prior to and during storage and analysis.

Analytical Procedures

A quality laboratory with necessary technician experience can achieve good results with many different methods. The modified automated SFAA method using the McLeod microstill may be the method of choice for the most advanced laboratories, however global uniformity, availability and cost factors indicate that the analytical methods listed as "Primary" in the following table as are suggested.

TABLE OF PRIMARY AND ALTERNATE ANALYTICAL METHODS

Analyte	Method	Comments
Free Cyanide	AgNO ₃ titration	Preferred method For process solutions primarily above 1 mg/l LQL ₁ : 1 mg/l HCN(aq), CN ⁻ , Zn(CN) _x , parts of Cu(CN) ₄

Analyte	Method	Comments
	AgNO ₃ titration with potentiometric endpoint determination	Alternate method Precise method of endpoint determination Measures same species as primary method
	Micro diffusion of HCN from static sample into NaOH [ASTM D4282]	Alternate Method Close to "free cyanide"
	Ion Selective Electrode	Alternate Method Close to "free cyanide"
	Direct colorimetry	Alternate Method HCN(aq), CN _x , Zn(CN) _x , parts of Cu(CN) ₄ + ?
	Amperometric determination	Alternate Method Measures same species as primary method
WAD Cyanide	Manual distillation pH 4.5 + potentiometric or colorimetric finish [ISO/DIS 6703/2, DIN 38405 Part 13.2: 1981-02]	Preferred method LQL ₁ : 0.05 mg/l HCN(aq), CN _x , Zn/Cd/Cu/Ni/Ag(CN) _x Better results than ASTM method in presence of high copper concentration
	Amenable to chlorination (CN Total - non-chlorinatable part) [ASTM D2036-B, US-EPA 9010]	Alternate Method Measures same species as primary method
	SFIA in-line micro-distillation pH 4.5 + colorimetric finish [ASTM D4374]	Alternate Method Measures same species as primary method
	FIA In-line ligand exchange + amperometric finish [US-EPA OIA-1677]	Alternate Method Measures same species as primary method
	Picric Acid, Colorimetric determination	Alternate Method Measures same species as primary method
Total Cyanide	Manual batch distillation + titration/potentiometric or colorimetric finish [ISO/DIS 6703/1, DIN 38405 Part 13.1: 1981-02]	Preferred method LQL ₂ : 0.10 mg/l HCN(aq), CN _x , Zn/Cd/Cu/Ni/Ag/Fe(CN) _x , parts of Au/Co/Pt/Pd(CN) _x
	SFIA, in-line UV irradiation, micro-distillation + colorimetric finish [ASTM D4374]	Alternate Method Measures same species as primary method

1 LQL, Lower Quantitation Level, is defined as about 3 times Detection Level or 10 times the Standard Deviation at near blank level.

For these primary methods, the table also provides a Lower Quantification Level representing the concentration that all laboratories should be able to reliably determine. Laboratories with a proven record of working with alternative methods, such as those based on automated standard methods, should be encouraged to continue with those methods but should establish cross-references for each site by applying the suggested methods.

To insure that the mine receives quality analytical service, the chosen laboratory must:

- Have experienced staff perform the analyses.
- Be certified by the respective national accreditation body for all analytical methods.
- Have sound quality control procedures in place.
- Be able to prove the quality of their data by participation in proficiency tests.

Trained analysts and supervisory staff with an expertise in cyanide chemistry methods are critical to consistent and reliable results, as they are aware of the potential interferences inherent in each method. The preferred methods for analytical determination of the different types of cyanide are briefly summarized below:

Free Cyanide

The preferred method for the analytical determination of free cyanide is silver nitrate titration. Silver ions are added to the solution to complex the free cyanide ions. When all free cyanide is consumed as silver cyanide complex, the excess silver ions indicate the endpoint of the titration. The analytical equipment used for the titration is rather simple. To accurately determine the cyanide concentration, a normalized silver nitrate solution is dosed with a manual or automatic burette, which should be capable of measuring volumes to an accuracy of better than 0.005 ml.

Several techniques can be used for the endpoint determination. The easiest possibility is to use an indicator such as potassium iodide or rhodanine that changes color upon appearance of free silver ions. It is important that the first color change is used as endpoint indication because the silver ions tend to liberate cyanide ions from other complexes, which leads to a disappearance of the color. The potentiometric endpoint detection is a more accurate way to determine the endpoint as a more easily identified peak signal is produced.

Weak Acid Dissociable Cyanide

The preferred analytical method to determine weak acid dissociable cyanide is the distillation method according to ASTM or ISO/DIS. These methods create chemical conditions which allow the CNWAD to be liberated as dissolved hydrogen cyanide gas which is then carried in an air stream to a caustic soda absorption where the CNWAD appears as CNF. As the hydrogen cyanide is adsorbed in a much smaller volume than the original sample solution, the CNF concentration to be analyzed is typically at least 10 times higher than the original CNWAD concentration in the sample solution. The CNF concentration in the distillation product sample is then determined using silver nitrate titration as described above. The methods according to ASTM and ISO/DIS are similar. However, the results from ISO/DIS method are more accurate than those from the ASTM method for samples containing a high concentration of copper cyanide.

Total Cyanide

The preferred analytical method to determine total cyanide is the distillation method according to ASTM or ISO/DIS. The applied method is in principle very similar to the distillation method described for weak acid dissociable cyanide. However, strongly acidic conditions and elevated temperatures are required to liberate the cyanide ion from the stable cyanide complexes such as ferri- and ferrocyanides.

References

Complete descriptions of these analytical procedures can be found in the following references:

DIN 38405-13: 1981-02, German Standard Methods for the Analysis of Water, Waste Water and Sludge - Anions (Group D) -Determination of Cyanides (D13), German Standards (DIN Normen, Beuth Verlag GmbH, Burggrafenstr. 6, 10787 Berlin/Germany).

South African Water Quality Guidelines, Volumes 1-7, Department of Water Affairs and Forestry, 1996.

Standard Methods For The Examination Of Waters and Wastewater, APHA-AWWA-WEF, 20th Edition, Washington DC, 1998.

Water Quality - Determination of Cyanide -Part 1: Determination of Total Cyanide ISO/DIS 6703/1, International Organization of Standardization.

Water Quality -Determination of Cyanide -Part 2: Determination of Easy Liberated Cyanide ISO/DIS 6703/2, International Organization of Standardization.

USEPA "Methods and Guidance for Analysis of Water", United States Environmental Protection Agency (USEPA), June 1999.